

# Accelerated Weathering of Limestone: An Inexpensive Means of Capturing and Sequestering CO<sub>2</sub> at Coastal Sites

Greg H. Rau<sup>a,b</sup>, Kevin G. Knauss<sup>b</sup>, William H. Langer<sup>c</sup>, Ken Caldeira<sup>b</sup>

(L-103, LLNL, 7000 East Ave., Livermore, CA 94550; 925-423-7990, rau4@llnl.gov)

<sup>a</sup>Institute of Marine Sciences, University of California, Santa Cruz, CA 95064

<sup>b</sup>Energy and Environment Directorate, LLNL, Livermore, CA 94550

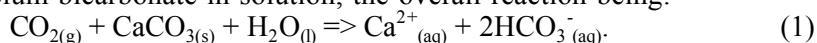
<sup>c</sup>US Geological Survey, Denver, CO 80225

## Abstract

Accelerated weathering of limestone (AWL) is evaluated as a low-tech, inexpensive, high-capacity, environmentally-friendly CO<sub>2</sub> capture and sequestration technology. The method involves hydrating point-source, waste CO<sub>2</sub> with seawater to produce a carbonic acid solution. This in turn is reacted and neutralized with limestone, thus converting the original CO<sub>2</sub> gas to dissolved calcium bicarbonate, the overall reaction being:  $\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \Rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ . With access to seawater and limestone being essential to this approach, it is shown that significant limestone resources are close to most CO<sub>2</sub>-emitting power plants along the coastal US. Waste fines, representing more than 20% of current US crushed limestone production (>10<sup>9</sup> tonnes/yr), could be used as an inexpensive source of AWL carbonate. Under such circumstances CO<sub>2</sub> mitigation cost could be as low as \$3-\$4/tonne CO<sub>2</sub> avoided. More broadly, 10-20% of US point-source CO<sub>2</sub> emissions could be treated at \$20-\$30/tonne CO<sub>2</sub>. AWL end-solution disposal in the ocean would significantly reduce effects on ocean pH and carbonate chemistry relative to those caused by direct atmospheric or ocean CO<sub>2</sub> disposal. Indeed, the increase in ocean Ca<sup>2+</sup> and bicarbonate offered by AWL could enhance growth of corals and other currently-threatened calcifying marine organisms. AWL is thus an attractive option for CO<sub>2</sub> mitigation because: 1) the reactants are inexpensive, abundant, and environmentally benign, 2) the technology is simple, low-cost, and amenable to power plant retrofitting, even in developing countries, 3) the storage is effective and long-term, and 4) the waste products are stable and have net positive environmental benefit.

## Introduction

The climate and environmental impacts of our current, carbon-intensive energy usage demands that effective and practical energy alternatives and CO<sub>2</sub> mitigation strategies be found.<sup>1,2</sup> As part of this effort, various means of capturing and storing CO<sub>2</sub> generated from fossil-fuel-based energy production are being investigated.<sup>3</sup> One of the proposed methods involves a geochemistry-based capture and sequestration process<sup>4,5</sup> that hydrates point-source, waste CO<sub>2</sub> with water to produce a carbonic acid solution. This in turn is reacted and neutralized with limestone, thus converting the original CO<sub>2</sub> gas to calcium bicarbonate in solution, the overall reaction being:



The dissolved calcium bicarbonate produced is then released and diluted in the ocean where it would add minimally to the large, benign pool of these ions already present in seawater.

Such a process is geochemically equivalent to continental and marine carbonate weathering which can otherwise naturally consume most anthropogenic CO<sub>2</sub>, but over many millennia.<sup>6-8</sup> We identify the enhanced form of this process as Accelerated Weathering of Limestone or AWL. Previously, it has been shown that AWL can effectively convert a significant fraction of US CO<sub>2</sub> emissions to long-term storage as bicarbonate in the ocean, while avoiding or possibly reversing environmental impacts associated with either the ongoing passive or the proposed active injection of CO<sub>2</sub> into the ocean.<sup>5,9</sup> Being analogous to the wide-spread use of wet limestone to desulfurize flue gas, AWL reactors could be retrofitted to many existing coastal power plants at a typical cost estimated to be \$20-\$30/tonne CO<sub>2</sub> mitigated.<sup>4,10</sup>

## Limestone and Seawater Availability and Cost

Based on reaction 1, it would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react 1 tonne of CO<sub>2</sub> to form 2.8 tonnes of HCO<sub>3</sub><sup>-</sup> in solution. It is envisioned that abundant and

inexpensive limestone (containing 92-98%  $\text{CaCO}_3$ ) would be used. US production of this mineral is presently  $10^9$  tonnes/yr, with reserves sufficient to satisfy US demand for many decades if not centuries. Channeling the entire yearly US limestone production to AWL could consume roughly 18% of the annual  $\text{CO}_2$  generated by electricity production in the US. However, currently more than 20% of US limestone production and processing results in waste limestone fines (<10 mm) that have little or no market value and are accumulating at limestone mining and processing sites.<sup>11,12</sup> This suggests that a sizeable, free or low-cost source of limestone could be available for AWL whose use could also help alleviate the significant limestone waste problem.

Because of the significant quantities of water required to react the  $\text{CO}_2$  and to carry and dilute the resulting bicarbonate ( $>10^4$  tonnes  $\text{H}_2\text{O}$ /tonne  $\text{CO}_2$ ; ref. 4), AWL reactors in close proximity to seawater would be at a distinct advantage. About 12% of  $\text{CO}_2$  emissions from US electricity production occurs at plants within 10 km of the US coastline.<sup>10</sup> Fortuitously, the majority of this coastline is also within 400 km of known limestone reserves.<sup>13</sup> This is especially true of the southern and eastern seaboard that also has the highest density of coastal US power plants and coastal electricity-related  $\text{CO}_2$  production. For example there is more than 20 GW of fossil-fueled power generation ( $\approx 100$  million tonnes  $\text{CO}_2$  emitted/yr) by coastal power plants in Florida<sup>10</sup>, a state that is almost entirely underlain by carbonate deposits.<sup>14</sup>

In such ideal settings, if both limestone and its transportation costs were negligible, the  $\text{CO}_2$  mitigation cost offered by AWL could be \$3 - \$4/tonne  $\text{CO}_2$  based on previous cost analyses.<sup>4,10</sup> This would especially pertain if the hundreds of millions of gallons of seawater already pumped and used for cooling by these plants each day were in turn used as a “free” AWL water source. This  $\text{CO}_2$  mitigation cost is significantly lower than most other current or proposed abiotic technologies.<sup>3</sup> However, the number of ideal sites and hence the volume of  $\text{CO}_2$  that could be treated at this very attractive cost would be small. Considering water, limestone, and transportation cost in more typical coastal settings suggests that 10-20% of US energy  $\text{CO}_2$  emissions could be mitigated at \$20-\$30/tonne.<sup>4,10</sup> This is still very cost-competitive with other methods, especially considering that the cost of conventional amine  $\text{CO}_2$  capture (not required for AWL) alone is generally  $> \$30$ /tonne  $\text{CO}_2$  (ref. 15).

The preceding assumes an AWL reactor sited at the source of waste  $\text{CO}_2$  (i.e. a power plant) and to which limestone and seawater are transported. Alternatively,  $\text{CO}_2$  generated at inland locations could be transported to coastal AWL reactors sited at or near limestone quarries. Transport of  $\text{CO}_2$  is inexpensive ( $\$0.06 \text{ tonne}^{-1} \text{ km}^{-1}$ , ref. 16) relative to the cost of transporting the AWL-equivalent (2.5 tonnes) of limestone. However, this would require initial  $\text{CO}_2$  separation, capture, and liquefaction, with the associated technology and energy costs that are presently significant, as mentioned above. Still, if inexpensive  $\text{CO}_2$  capture/separation is developed, piping  $\text{CO}_2$  to coastal AWL reactors could prove cost-competitive with other forms of  $\text{CO}_2$  sequestration such as underground storage, especially in regions where the underlying geology is not amenable to  $\text{CO}_2$  retention.

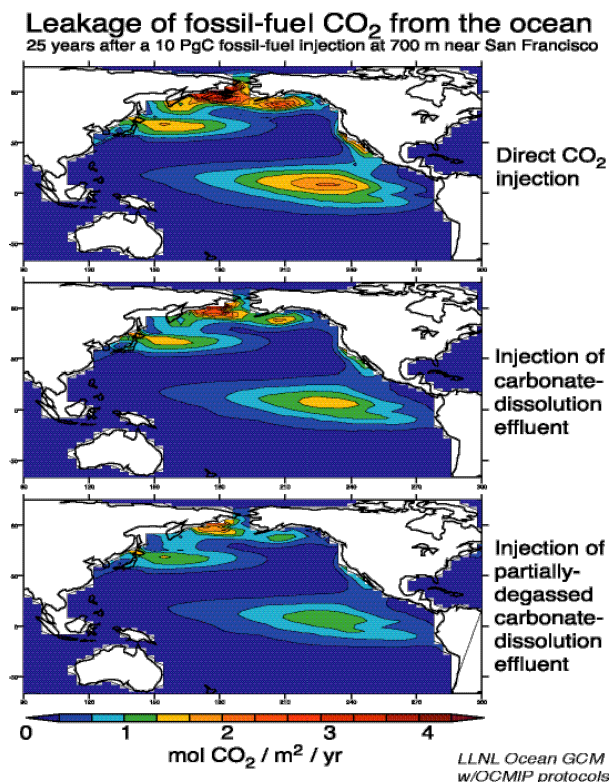
### Reaction Rates and Densities

The results of experiments in our laboratory yielded limestone dissolution rates ranging from roughly  $10^{-7}$  to  $10^{-5}$  moles  $\text{m}^{-2} \text{ s}^{-1}$  with positive sensitivity to flow rate, stir rate, and  $\text{CO}_2$  concentration. Dissolution rates in seawater were equal to or higher than those in distilled water under otherwise identical conditions.

Assuming a reaction rate of  $10^{-6}$  moles  $\text{m}^{-2} \text{ s}^{-1}$  is achievable in large-scale reactors, a bed of 1mm-diameter limestone particles (typical of waste limestone fines discussed above) yields a surface area/volume of  $\geq 4.4 \times 10^3 \text{ m}^2/\text{m}^3$ . Therefore a maximum of 60  $\text{m}^3$  of such limestone particles would be needed to react 1 tonne of  $\text{CO}_2$  per day. For a cubic reactor volume (roughly 4m x 4m x 4m), this equates to an areal reaction rate of at least 15 tonnes  $\text{CO}_2 \text{ m}^{-2} \text{ day}^{-1}$ , or about a million times greater than optimum biotic  $\text{CO}_2$  uptake and sequestration rates.<sup>16</sup> The experiments suggest that this density of  $\text{CO}_2$  conversion to  $\text{HCO}_3^-$  could be increased by as much as an order of magnitude by increasing stirring and flushing rate, though at added energy and cost penalties.

## Effectiveness

Using a box model of ocean chemistry and transport, Caldeira and Rau<sup>5</sup> showed that the release of the bicarbonate-charged effluent from carbonate dissolution would more effectively sequester CO<sub>2</sub> over the long term than direct CO<sub>2</sub> injection at equivalent ocean depths. This has been subsequently confirmed for releases at several different ocean locations and depths in a 3-D ocean general circulation model (**Figure 1**). Injection of pure CO<sub>2</sub> at great depth in the ocean effectively stores most of the injected carbon for hundreds of years or more.<sup>5</sup> Therefore, the additional slowing of CO<sub>2</sub> leakage that would be gained by releasing carbonate dissolution effluent at the same depth may not be economically significant. Nevertheless, we note that carbonate dissolution can make a major contribution for less costly shallow-water releases and greatly improves effectiveness of long-term ocean carbon sequestration regardless of the depth at which the effluent is released.



**Figure 1.** Ocean general circulation model results showing the greater effectiveness (less CO<sub>2</sub> leakage to atmosphere) inherent in the injection of carbonate dissolution effluent as compared to molecular CO<sub>2</sub> at equivalent depths.

## Environmental Impacts/Benefits

An increase in ocean acidity (reduction in pH) is a serious environmental issue caused either by the ongoing diffusive uptake of anthropogenic CO<sub>2</sub> from the atmosphere or the proposed purposeful injection of CO<sub>2</sub> into the ocean.<sup>9</sup> Storing waste CO<sub>2</sub> in the form of bicarbonate ions balanced by Ca<sup>2+</sup> rather than by H<sup>+</sup> (i.e., as carbonic acid) substantially lessens the increase in acidity per tone of carbon added to the ocean, while reducing harmful effects to marine biota of direct ocean CO<sub>2</sub> additions.<sup>17,18</sup> In fact, Ca<sup>2+</sup> and bicarbonate enrichment of seawater has been shown to significantly enhance the calcification and growth rate of marine corals.<sup>19,20</sup>

Nevertheless, negative marine environmental impacts could result via reduction in oxygen concentration in the effluent through partial equilibration with flue-gas streams. As well, impurities released into the effluent solution from the limestone or the flue gas could be biotically impactful. Experimentation is required to quantify such effects. We point out, however, that the ocean naturally receives and accommodates about 2 x 10<sup>9</sup> tonnes of dissolved calcium bicarbonate per year produced from continental carbonate weathering as delivered by rivers.<sup>21</sup>

We also note that limestone is already widely used for environmental benefit, flue gas desulfurization and acid mine waste neutralization being prime examples.

## Conclusions

In the appropriate settings AWL is an attractive option for CO<sub>2</sub> mitigation because: 1) the required reactants are relatively inexpensive, abundant, and environmentally benign, 2) the technology is relatively simple, low-cost, and amenable to power plant retrofitting, even in developing countries, 3) the storage is effective and long-term, and 4) the waste products are stable and appear to have net positive environmental benefit. All of these features derive from the fact that AWL merely enhances Nature's own CO<sub>2</sub> capture and sequestration mechanism, carbonate weathering. More research is needed, however, to more accurately assess the costs, benefits, and impacts of this means of mitigating CO<sub>2</sub> from point sources.

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